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CITY OF PORTSMOUTH, NEW HAMPSHIRE Background Water Quality Sampling in Support of the Future Pease NPDES Permit

DRAFT Quality Assurance Field Sampling Plan
May 23, 2018

Portsmouth Background Water Quality Sampling Quality Assurance and Field Sampling Plan

Underwood Engineers, Inc.
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Introduction

The City of Portsmouth requires water quality sampling in the Piscataqua River near the Pease and Newington Wastewater Treatment Facility (WWTF) combined discharge outfall. Results from this sampling effort will provide data to the City and New Hampshire Department of Environmental Safety (NHDES) in support of making decisions on the future Pease National Pollutant Discharge Elimination System (NPDES) permit capacity and to support an Antidegradation Water Quality Study that will be performed by NHDES. This monitoring effort consists of sampling in the Piscataqua River upstream of the Pease and Newington Outfall. Concurrent effluent sampling will be performed at the Pease and Newington Wastewater Treatment Facilities. The WWTF effluent sampling includes 24-hour flow-weighted composite samples and effluent grab samples to fully characterize the water quality flows from the WWTFs to the Piscataqua River. The data will be summarized in a sampling report for submittal to the City and NHDES

This Quality Assurance and Field Sampling Plan (QAFSP) includes a discussion of the sampling plan rationale, sampling locations and figures, program management, a detailed list of analytical parameters, standard operating procedures, and the reporting framework. The QAFSP follows quality assurance (QA) and quality control (QC) measures detailed in this document.

1. Sampling Plan Rationale

This sampling program consists four (4) rounds of concurrent sampling at three (3) unique locations. Table 1 lists the sampling locations, the type of sampling that will be conducted, and category of analytical parameters. (The parameter categories are further explained in Section 3.1, Table 4.) The results of this study will provide data on the current water quality characteristics of the Piscataqua River during low flow conditions and the effluent water quality of both the Pease and Newington wastewater treatment facilities (WWTFs).

Table 1: Location and description of samples taken during this study.

Sampling Location	Sample Type	Parameters
Diagotogue Divor	Grab Sample	Laboratory
Piscataqua River	In-Situ Measurements	Field
D WWTE ECO	24-hour Flow-Weighted Composite	Laboratory
Pease WWTF Effluent	Grab Sample	Field
NI - ' XXXX/PP POI	24-hour Flow-Weighted Composite	Laboratory
Newington WWTF Effluent	Grab Sample	Field

Piscataqua River Sampling

The Piscataqua River (River) sampling will be in the zone upstream of the Pease and Newington wastewater treatment facility combined outfall. Upstream in this situation is south of the outfall towards the ocean as the sampling will be conducted during the flood tide. The objective of the sampling is to measure background water quality during a tidal stage when the dilution of all sources of pollution, including contributions from the WWTFs, is at or near the lowest levels.

River sampling will be conducted during low flow conditions targeting the low to high tidal cycle during June and July of 2018. Based on NHDES guidance the difference between the low to high tide must be less than 6.5 feet and the grab samples must be taken 1.5 hours after local slack low tide. River samples be taken from a boat approximately 200 to 300 feet upstream of the WWTF outfalls (Figure 1) to minimize outfall and nearshore interferences imples will be taken below the water surface avoid possible floating material and boat interferences. Additional in-situ measurements using water quality meters will be conducted to record field parameters i.e. dissolved oxygen, temperature, pH, and conductivity (salinity) levels at the time of sampling. A total of four (4) sampling events have been identified that meet these criteria during June and July 2018 and are listed in Table 2. Backup dates will be selected in the event that sampling efforts are unsuccessful due to rainfall occurrences, equipment failure, unsafe river conditions, WWTF issues, or other unforeseen circumstances.

Table 2: Details of sampling events in Piscataqua River

Date	Day	Time	Tide Height (ft)	Approximate River Sampling Time
6/6/2018	Wed	11:49	6.12	13:19
7/3/2018	Tue	21:56	6.27	23:26
7/8/2018	Sun	01:22	6.37	02:52
7/23/2018	Mon	03:12	6.49	04:42

Wastewater Treatment Facility Sampling

Sampling of the Pease and Newington WWTF's effluent will consist of 24-hour flow-weighted composite samples and grab samples. The flow-weighted composites will be generated over the 24-hour period, 8am to 8am, ending on the day of the river sampling. Table 3 lists the details of these sampling events. The flow-weighted composite samples will be generated using preprogrammed automated samplers that will take a predetermined sample aliquot after a specified volume of effluent water has passed the monitoring location. All aliquots are dispensed into a single 5.5-gallon container that is housed in a temperature-controlled compartment within the sampler. The purpose of a flow-weighted composite sample is to develop an aggregate concentration over the specified monitoring period that accounts for fluctuations in the effluent flow. At the end of the 24-hour period these samples are processed and shipped for laboratory analysis in accordance with sample processing protocols detailed in this QAFSP. The WWTF grab samples are taken at the end of each 24-hour composite sampling period and analyzed at the in-house WWTF lab for field parameters, i.e. dissolved oxygen, temperature, pH, and conductivity (salinity).

Table 3: Details of concurrent sampling events at Pease and Newington wastewater treatment facilities.

COMPOSITE SAMPLES					CDA	B SAMI	DIEC	
Start				End			D SAIVLI	rles
Date	Day	Time	Date	Day	Time	Date	Day	Time
6/5/2018	Tues	08:00	6/6/2018	Wed	08:00	6/6/2018	Wed	08:00
7/2/2018	Mon	08:00	7/3/2018	Tue	08:00	7/3/2018	Tue	08:00
7/6/2018	Fri	08:00	7/7/2018	Sat	08:00	7/7/2018	Sat	08:00
7/21/2018	Sat	08:00	7/22/2018	Sun	08:00	7/22/2018	Sun	08:00

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26" HDPE Outfall 4" Risers 8 – 4" 45° Tide Flex Approximate location of river sampling (~200-300 ft.) lewington WWTF 8,300 ft 27" RCP Atlantic Heights Pease WWTF CORPORATE SELVERS

PEASE WWTF - LOCATION OVERVIEW

Figure 1: Map of WWTF locations, outfall pipe, and Piscataqua River sampling location.

1.1 Sampling Strategy

Sampling in the River and at both WWTFs will consist of the primary samples as well as quality control (QC) samples. The first round of sampling will include the full suite of QC samples for all locations consisting of field duplicates for laboratory parameters and field replicates for field parameters. In addition, trip blanks, equipment blanks, and matrix spike / matrix spike duplicates (MS/MSD) will be analyzed for metals, cyanide, total phenolic compounds, volatile organic compounds, acid extractable compounds, and base-neutral compounds. Sampling rounds 2 through 4 will have a reduced count of QC samples consisting of field duplicates at each location for ammonia as N, total Kjeldahl nitrogen, nitrate plus nitrite nitrogen, total phosphorus, and metals; field replicates at each location for field parameters; equipment blanks and MS/MSD analyzed for metals at each location. In addition, trip blanks of River samples will be analyzed

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for cyanide, total phenolic compounds, volatile organic compounds, acid extractable compounds, and base-neutral compounds. Tables of each round of sampling, QC samples, testing parameters, and the total project sample counts can be found in Appendix A of this QAFSP.

The River sampling will be conducted in accordance with the standard grab sampling protocol outlined in Appendix B. The in-situ measurements will adhere to the standard protocol for collection of water quality data with multi-parameter water quality meters outlined in Appendix C. Special attention will be given during field sampling activities to avoid obvious sources of metals contamination and to avoid protocols that could introduce metals contamination. Wherever possible, non-metal instruments and equipment will be used.

The River grab samples will be collected by boat (19' fiberglass, gas fueled) from just below the surface avoid possible floating debris. The boat will be anchored and 3-5 min of water flow will be allowed prior to any sampling or measurements. Whenever possible, samples will be collected facing upstream and upwind to minimize introduction of contamination. The grab samples will be collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter. The grab samples will be collected using the "Clean Hands" technique (EPA Method 1669 - Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels) as outlined in Appendix D. QC sample requirements are summarized in Appendix A and discussed in Section 4.2.

The samples will be picked up by EnviroSystems laboratory personnel and delivered to Hampton, New Hampshire for the required analyses. Sampling details including sample date, sample time, analytical parameters, and preservation type will be recorded on the chain-of-custody (COC) form (Appendix E). Chain-of-custody protocol will be followed during any transfer of the samples (i.e., from City personnel to Underwood Engineers staff and from Underwood Engineers staff to EnviroSystems staff). River samples that will be analyzed for trace metals will be filtered in the field following trace metals sample handling protocols outlined in Appendix D. Samples prepared for trace metals analysis will be packaged and shipped to Eurofins Frontier Global Sciences in Bothell, Washington.

The in-situ field measurements will be conducted using a multi-parameter water quality meter (i.e., YSI 6600 or equivalent) to record measurements of dissolved oxygen, temperature, pH, and conductivity (salinity). Field data will be recorded using the field meter as well as recorded in a field notebook. Details of the YSI 6600 are included in Appendix C. The water quality meter will be calibrated by field personnel prior to and following each sampling round following the manufacturer's standard protocols. Field replicates consisting of two or more field measurements collected sequentially while in the field will be conducted to assess the precision of the measurements in relation to the instrument variability and sampler error, as well as changing water conditions with flowing tidal water. Replicate values will be recorded in the field notebook.

The WWTF effluent sampling by the City personnel will be conducted in accordance with their own standard sampling protocols and adhere to the standard level of quality assurance and quality control measures. The WWTF effluent sample will consist of a 24-hour composite sample collected during the 24-hour period prior to the planned River sampling time as detailed

Portsmouth Background Water Quality Sampling Ouality Assurance and Field Sampling Plan in Table 3. WWTF grab samples will be collected at the completion of the 24-hour composite sample timeframe, delivered to EnviroSystems, and analyzed for the following laboratory parameters: fecal coliform, enterococci, total residual chlorine, oil and grease, turbidity, and VOC. Additional grab samples will be collected for the following field parameters: dissolved oxygen, temperature, pH, and conductivity (salinity) and measured at the WWTF. Replicate field measurements will be recorded for verification of results.

WWTF composite and grab samples will be picked up by Underwood Engineers personnel at the WWTF, packaged with the River samples, and delivered to either EnvironSystems or Eurofins Frontier Global Sciences for analyses. See Table 4 for the project sample matrix detailing sampling location, analytical parameters, and analytical laboratory.

2. Sampling Locations

Figure 1 above depicts the locations of the Newington and Pease WWTFs, the combined WWTF outfall, and the Piscataqua River sampling location. The sampling locations are listed as follows:

- 1. Pease WWTF Effluent 24-hour composite sample referred to as PEASE 001C
- 2. Pease WWTF Effluent grab sample referred to as PEASE 001G
- 3. Newington WWTF Effluent 24-hour composite sample referred to as NEW 001C
- 4. Newington WWTF Effluent grab sample referred to as NEW 001G
- 5. Piscataqua River grab sample referred to as RIVER 001G

3. Program Management and Organization

The project organization chart is included as Figure 2. Team members include staff from the City of Portsmouth Department of Public Works, Underwood Engineers, Eurofins Frontier Global Sciences, and EnviroSystems. A summary of the key personnel along with their primary responsibilities is presented below:

- Mr. Terry Desmarais (P.E.) is the lead contact for the project for the City of Portsmouth Department of Public Works. Mr. Desmarais will be responsible for approving this QAFSP and coordinating all project efforts.
- Mr. Ricardo Cantu
- Mr. Patrick Wiley (Ph.D.) is the wastewater operations manager for the City of Portsmouth Department of Public Works. Mr. Wiley will be responsible for...
- Ms. Paula Anania is the chief plant operator for the City of Portsmouth Wastewater division. Ms. Anania will be responsible for...
- Mr. Denis Messier
- Mr. Steve Clifton (P.E.) of Underwood Engineers will be the project manager and will be responsible for ensuring that all field data and samples are collected in accordance with this QAFSP. Mr. Clifton will be responsible for review and submittal of all deliverables required under this project.
- Mr. Tim Puls (P.E.) of Underwood Engineers will be the field project manager. Mr. Puls will be responsible for preparation of the QAFSP and for coordinating the field schedule of the sampling program.

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- Ms. Amanda Komarek will be the primary laboratory contact at EnviroSystems. Ms. Komarek will be responsible for ensuring that the appropriate sample bottles are delivered to both Underwood Engineers and the City of Portsmouth for their respective sampling, for ensuring that all samples are received by the laboratory in accordance with QAFSP requirements, and for confirming that the laboratory reports are provided to Underwood Engineers following each sampling round.
- Mr. Robert Brunette will be primary laboratory contact at Eurofins Frontier Global Systems. Mr. Brunette will be responsible for ensuring sampling equipment (i.e. tubing, vacuum filters, and sample containers) has been cleaned in accordance with trace metal sampling protocols and delivered to Underwood Engineers. Mr. Brunette will also be responsible for ensuring all samples are received by Eurofins in accordance with QAFSP requirements and for providing laboratory reports to Underwood Engineers following each sampling round.

Figure 2: <TEAM ORGANIZATION CHART>

4. Sampling Parameters and Sampling SOPs

Sampling of Piscataqua River and the Pease and Newington WWTFs effluent will involve collection of grab samples, generation of 24-hour composite samples, and in-situ measurements. Samples will be analyzed for either laboratory or field parameters by one of two analytical laboratories, field sampling personnel, or WWTF personnel. Coordination of sample collection, field processing, packaging, and delivery to the respective labs will be conducted by Underwood Engineers. The project sample matrix including analytical methods is listed in Table 4.

Table 4: Project sample matrix including analytical parameters, sample source, analytical method,

and entity responsible for testing.

and entity responsible for testing.							
SAMPLE MATRIX							
Laboratory Parameter	River	WWTF	Analytical Method	 			
Biochemical Oxygen Demand (BOD5)	Grab	24-hour Comp	SM 5210 B	EnviroSystems			
Enterococci & Fecal Coliform	Grab	Grab	SM 92222 D	EnviroSystems			
Total Suspended Solids (TSS)	Grab	24-hour Comp	SM 2540 D	EnviroSystems			
Total Dissolved Solids (TDS)	Grab	24-hour Comp	SM 2540 C	EnviroSystems			
Ammonia as N (NH3-N)	Grab	24-hour Comp	SM 4500-NH3 G	EnviroSystems			
Chlorine (Total Residual)	NA	Grab	SM 4500-Cl D	EnviroSystems			
Total Kjeldahl Nitrogen (TKN)	Grab	24-hour Comp	SM 4500-NH3 G	EnviroSystems			
Nitrate + Nitrite as Nitrogen	Grab	24-hour Comp	SM 4500-NO3 F	EnviroSystems			
Oil and Grease	Grab	Grab	EPA 1664 A	EnviroSystems			
Total Phosphorus	Grab	24-hour Comp	SM 4500-P E	EnviroSystems			
Turbidity (NU)	Grab	Grab	SM 2130 B	EnviroSystems			
Total Phenols	Grab	24-hour Comp	EPA 420.1	EnviroSystems			
Volatile Organic Compounds	Grab	Grab	EPA 624	EnviroSystems			
Acid-Base-Neutral Extractable Compounds (ABNs)	Grab	24-hour Comp	EPA 625 / 8270	EnviroSystems			
Total Recoverable Metals (Sb, As, Be, Cd, Cr, Cu,			EPA 200.8 CWA				
Fe, Pb, Ni, Se, Ag, Tl, Zn)	NA	Gral (iltered)	Trace Metals	Eurofins FGS			
Total Hg	NA	Grab (unfiltered)	EPA 1631 E	Eurofins FGS			
Total Cn	NA	Grab (unfiltered)	SM 4500-Cn E	Eurofins FGS			
			EPA 200.8 CWA				
Total Recoverable Metals (Sb, Be, Cr, Fe, Tl)	Grab (unfiltered)	NA	Trace Metals	Eurofins FGS			
Dissolved Metals (As, Cd, Cu, Pb, Ni, Se, Ag, Zn)	Grab (filtered)	NA	EPA 1640 RP	Eurofins FGS			
Total Cn	Grab (unfiltered)	NA	Pending	Eurofins FGS			
Dissolved Hg	Grab (filtered)	NA	EPA 1631 E	Eurofins FGS			
Field Parameter							
Dissolved Oxygen	In-Situ	Grab		Field Team/WWTF			
Temperature	In-Situ	Grab		Field Team / WWTF			
pН	In-Situ	Grab		Field Team / WWTF			
Conductivity	In-Situ	Grab		Field Team / WWTF			

4.1. Metals Sampling and Analysis

Special attention is given to sample collection and analysis of total recoverable and dissolved metals. Selection of Eurofins Frontier Global Sciences (Eurofins) for all metals testing is based on their capacity to conduct trace metals techniques. Eurofins will conduct metals testing in accordance with EPA Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, Appendix D. Field sampling will also adhere to Method 1669 criteria which requires all sampling equipment and sample containers are cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water. These techniques are required to obtain the minimum reporting limit and minimum detection limits achievable. Most of the metals listed have minimum marine acute and chronic criteria levels based on NHDES Env-Wq rule 1703.21 Water Quality Criteria for Toxic Substances. An excerpt from Table 1703-1 is included as Table 5, which lists the acute and chronic criteria levels for both fresh and marine waters for the target parameters.

Table 5: Excerpt from Table 1703-1 in NHDES Env-Wq rule 1700 Surface Water Quality Standards

Table 1703-1: Water Quality Criteria For Toxic Substances

Tuble 1703-1. Water Guality Criteria For Toxic Substances									
		Protection of Aquatic Life				Protection of Human			
CAS	Chemical	Concentra	Concentration in micrograms per liter (µg/l)				Health Units per Liter		
Number	Name	Fresh	Fresh	Marine	Marine	Water &	Fish		
Number	Name	Acute	Chronic	Acute	Chronic	Fish	Consumption		
		Criteria	Criteria	Criteria	Criteria	Ingestion	Only		
7440360	Antimony	9,000	1,600			5.6 µg	640 µg		
7440382	Arsenic	340	150	69	36	18 ng	140 ng		
7440417	Beryllium	130	5.3			Note 1			
7440439	Cadmium	0.39	0.21	33	7.9	Note 1			
16065831	Chromium	152	19.8	10,3000	==	Note 1			
	+3								
7440508	Copper	2.9	2.3	4.8	3.1	1,000 μg	1,000 μg		
57125	Cyanide	22	5.2	1.0	1.0	140 μg	140 μg		
7439896	Iron		1,000			0.3 mg			
7439921	Lead	10.5	0.41	210	8.1				
7439976	Mercury	1.4	0.77	1.8	0.94	0.05 μg	0.051 μg		
7440020	Nickel	120	13.3	74	8.2	610 µg	4,600 μg		
7782492	Selenium		5	290	71	170 μg	4,200 μg		
7440224	Silver	0.20		1.9	==	105 μg	65 mg		
7440280	Thallium	1,400	40	2,130		0.24 μg	0.47 μg		
744066	Zinc	30.0	30.0	90	81	5,000 μg	5,000 μg		

4.2. Quality Assurance for Data Collection and Analyses

Quality control tasks involve planning for the type and number of quality control samples to be collected as well as several routine technical activities. The technical activities include but are not limited to:

- Calibration of field instruments according to manufacturer's specifications and record of calibrations results in field notebooks
- Preparation of field sample bottles (e.g., rinsed, sterilized, preservative added, cleaned in accordance with EPA Method 1669 for metals, etc.) prior to sample collection
- Preparation of field data sheets and log books
- Preparation of sample labels

A general overview of water quality monitoring sampling protocols can be found in Appendix F by the NH Volunteer River Assessment Program, which provides information on proper preparation of sample containers and the preservation of samples.

4.2.1. Quality Control Samples

The type and number of QC samples has been established based on a total of four rounds of sampling at three monitoring locations, i.e. Piscataqua River, Pease WWTF, and Newington WWTF. See Appendix A for a detailed table of the sample types and counts that will be

collected for this project. The type of QC samples includes field duplicates for laboratory parameters, field replicates for field parameters, trip blanks, equipment blanks, matrix spike and matrix spike duplicates. For a detailed description and rationale of each QC sample type see Table 6. The number of quality control samples is consistent with EPA quality control guidance (The Volunteer Monitor's Guide to Quality Assurance Project Plans, September 1996, EPA 841-B-96-003) and the NHDES Ambient River Monitoring Program. See Section 1.1 of this QAFSP and Appendix A for additional detail on each sampling round.

Table 6: Description and rationale of quality control samples.

Quality Control Sample Type	Sample Description	Rationale
Equipment Blank	Blank (deionized) water passed through equipment in the field and collected in the same manner used to collect water quality samples.	To verify that decontamination procedures are adequate and that field and laboratory protocols and procedures do not contaminate samples.
Trip Blank	Blank (deionized) water placed in sample container by the laboratory, carried to the study site with other bottles and equipment, and returned to the laboratory unopened for analysis.	To verify that the shipping, handling, and intermittent storage of containers does not result in contamination or cross-contamination of samples
Duplicate Sample	Two water quality samples collected sequentially for the same analytes.	To assess the combined effects of field and laboratory procedures on the measurement variability.
Replicate Sample	Two or more field sample measurements (dissolved oxygen, temperature, pH, conductivity) collected sequentially while in the field.	To assess the precision of measurement in relation to instrument variability and sampler error
Spike Matrix	A sample of either river or WWTF effluent water to which a spike solution is added (spikes will be for metals).	To assess the recovery bias and variability in relation to different water matrices.

4.2.2. Data Management Tasks

All relevant field and laboratory data will be provided in a hard copy report and electronic form. The field data documentation will be recorded in field notebooks appropriate for the sampling location and will include the following:

- Date, time, and name of technician(s) present while conducting sampling
- Field equipment checklist to ensure all necessary equipment is present when initiating field sampling trips
- Site conditions i.e. weather, river condition, presence of excessive debris or unknown substances in water that may contaminate sample
- Record of recent rain events or antecedent dry period
- Disturbance in normal operations at WWTF that may influence sample

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For preservation, scanned copies of all handwritten field notes shall be made as soon as possible after each sampling event and saved on a database that can be accessed by the project manager.

4.2.3. Data Verification and Validation Tasks

Water quality data are verified by referencing replicate samples, reviewing critical ranges, reviewing consistency of spiked samples, and reviewing duplicate samples. The data are screened for outliers, with outliers being highlighted and examined to determine the cause of the deviation.

4.2.4. Measurement Performance Criteria for Water Quality Measurements

The measurement performance criteria for data associated with all matrices include considerations for precision, accuracy, representativeness, completeness, and comparability (PARCC). To meet PARCC requirements, quality control criteria are provided in the standard laboratory methodologies. These criteria include the use of field duplicates, field replicates, matrix spike samples, and calibration results to assess precision; calibration results, trip blanks, equipment blanks, and matrix spikes to assess accuracy and bias; blank samples to determine representativeness. The amount (percentage) of valid data obtained will be used to determine completeness.

An overview of the measurement performance criteria to be used in this study for water samples is listed in Table 7 and explained in more detail below it. The specific performance criteria goals and related information for each analyte/measurement are listed in Table 8.

Table 7: Data quality indicators (PARCC) requirements and measurement performance criteria.

Data Quality Indicators	Measurement Performance Criteria	RPD Value	QC Sample and/or Activity Used to Assess Measurement Performance
Precision-Overall	RPD	RPD ≤ 10%	Field Duplicates Field Replicates
Precision-Lab	RPD	RPD ≤ 10%	Matrix Spike Samples Sensor Calibration results
Accuracy / Bias	RPD	RPD ≤ 10%	Sensor Calibration Results Trip Blanks Field Blanks Laboratory Fortified Matrix Spikes
Representativeness	Adherence to field and lab protocols	RPD ≤ 10%	Field Duplicates Field Replicates
Comparability	Measurements should follow standard methods that are repeatable		All project personnel will review QAFSP and previous City of Portsmouth Water Quality Study, 2014
Completeness	Number of samples meeting data quality objectives		Data Completeness Check > 90% valid water quality results

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Precision

Field duplicates or field replicates are collected for all parameters for the first sampling round and for select parameters for each successive sampling round (Appendix A). Field duplicates are physical water quality duplicate samples to assess environmental variability as well as strict adherence to field sampling and laboratory techniques. Field replicates are repeated measurements to assess instrument variability using water quality sensors.

Precision goals vary according to specific pollutant but should remain within a threshold of 10% relative percent difference. The relative percent difference (RPD) will be calculated as follows:

$$RPD = \left(\frac{\left|\underline{x}_1 - \underline{x}_2\right|}{\frac{\underline{x}_1 + \underline{x}_2}{2}}\right) \times 100$$

where the equation numerator is the absolute value of the difference between duplicates and denominator is the average of the duplicates. RPD will be calculated for each set of duplicates and replicates for each round of sampling and reported to the City.

Accuracy

The water quality sensors calibration accuracy will be checked against standard solutions prior to each usage. If the standard solution is not measured within $\pm 10\%$ RPD of the known value the instrument will be recalibrated prior to field use. A two-point calibration procedure will be used, as specified by the manufacturer of the instrument to encompass the range of values typically encountered in similar systems. All calibration data will be documented in the field log books.

Trip blanks are deionized water aliquots that are bagged and sealed according to standard sampling protocols (Table 6) and brought into the field to assess contamination from typical field sampling procedures. For data to be precise and credible trip blanks should return below or at analytical detection limits 100% of the time.

Equipment blanks are collected at least one sampling event and consist of distilled water aliquots that are conveyed through existing sampling equipment under field conditions and are analyzed to detect any contamination from sampling methodology, and cross-contamination from previously collected samples. For data to be precise and credible, equipment blanks should return below or at analytical detection limits 100% of the time.

Representativeness

Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population at a sampling point or for a process condition or environmental condition. Representativeness is achieved through the consistent use of documented procedures for field sampling and handling process and through consistent adherence to laboratory methods.

Many water quality parameters are spatially and temporally dynamic, and experience near-limiting ambient conditions (e.g., low stream flow, warm water temperature) typically during the summer. For example, dissolved oxygen concentrations are typically least during the early morning hours in response to photosynthetic/respiration cycles. Decisions as to sampling

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location and time will represent the water quality parameters of interest in their expected abundance in the sample.

Comparability

Consistent data collection techniques and analytical parameters will support meaningful comparisons of gathered data. Water quality data will be compared to results in a previous related study, City of Portsmouth Peirce Island Wastewater Treatment Facility and Piscataqua River Water Quality FINAL Report, September 2014. A comparison of the water quality results and the laboratory and field sampling protocols followed for each monitoring effort will help to inform the repeatability of the study. For this project, comparability is attempted through the use of similar field sampling procedures, analytical methods, certified calibration standards, and representative sampling locations.

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements expected to be obtained under normal conditions. For analytical methods, completeness is based on the number of valid results generated over a specific period compared to the number of results expected.

The quality objective for completeness for analyses performed by the analytical laboratory is 90-95 percent valid data for water quality results, collected during four (4) sampling rounds at each location for each sample type, for the analytes listed in Table 4. The ability to meet or exceed the completeness objective is dependent on the nature of samples submitted for analysis.

4.2.5. Quantification Limits

Each analytical method has a method detection limit (MDL) and method reporting limit (MRL), which are defined as follows and listed in Table 8.

Method Detection Limit (MDL)

The smallest concentration of analyte which may be detected by the entire analytical method including any sample preparation steps. It may be determined using replicate spike samples or calibration standards. The detection limit is calculated using the appropriate student's t parameter times the standard deviation of a series of spiked samples or standards. The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. (Absolute Resource Associates, Lab QA Manual, 2004)

Method Reporting Limit (MRL)

The lowest amount of an analyte in a sample that can be quantitatively determined with stated, acceptable precision and accuracy under stated analytical conditions (i.e. the lower limit of quantitation). Therefore, analyses are calibrated to the MRL, or lower. To take into account day-to-day fluctuations in instrument sensitivity, analyst performance, and other factors, the MRL is established at three times the MDL (or greater). (www.caslab.com)

Table 8: Method detection limit (MDL) and method reporting limit (MRL) for all target

parameters in this project.

parameters in this project.	Amalestical			
Laboratory Parameter	Analytical Method	MDL	MRL	Units
Biochemical Oxygen Demand (BOD5)	SM 5210 B			
Enterococci & Fecal Coliform	SM 92222 D			
Total Suspended Solids (TSS)	SM 2540 D			
Total Dissolved Solids (TDS)	SM 2540 C			
Ammonia as N (NH3-N)	SM 4500-NH3 G			
Chlorine (Total Residual)	SM 4500-Cl D			
Total Kjeldahl Nitrogen (TKN)	SM 4500-NH3 G			
Nitrate + Nitrite as Nitrogen	SM 4500-NO3 F			
Oil and Grease	EPA 1664 A			
Total Phosphorus	SM 4500-P E			
Turbidity (NU)	SM 2130 B			
Total Phenols	EPA 420.1			
Volatile Organic Compounds	EPA 624			
Acid-Base-Neutral Extractable Compounds				
(ABNs)	EPA 625 / 8270			
Total Recoverable Metals - Fr	esh Water (CWA Tra	ce Metals)	,	
Antimony (Sb)	EPA 200.8	0.009	0.02	μg/L
Arsenic (As)	EPA 200.8	0.1	0.3	μg/L
Beryllium (Be)	EPA 200.8	0.004	0.06	μg/L
Cadmium (Cd)	EPA 200.8	0.008	0.02	μg/L
Chromium+3 (Cr3)	EPA 200.8	0.02	0.1	μg/L
Copper (Cu)	EPA 200.8	0.02	0.1	μg/L
Iron (Fe)	EPA 200.8	1.1	10	μg/L
Lead (Pb)	EPA 200.8	0.005	0.04	μg/L
Nickel (Ni)	EPA 200.8	0.04	0.1	μg/L
Selenium (Se)	EPA 200.8	0.44	0.6	μg/L
Silver (Ag)	EPA 200.8	0.002	0.02	μg/L
Thallium (Tl)	EPA 200.8	0.006	0.02	μg/L
Zinc (Zn)	EPA 200.8	0.16	0.5	μg/L
Total Mercury (Hg)	EPA 1631 E	0.0834	0.5	ng/L
Total Cyanide (Cn)	SM 4500-Cn E	0.007	0.02	mg/L
Total Recoverable Metals - S	Seawater (CWA Trac	e Metals)		
Antimony (Sb)	EPA 200.8	0.09	0.2	μg/L
Beryllium (Be)	EPA 200.8	0.04	0.6	μg/L
Chromium+3 (Cr3)	EPA 200.8	0.2	1.0	μg/L
Iron (Fe)	EPA 200.8	11	100	μg/L
Thallium (Tl)	EPA 200.8	0.06	0.2	μg/L

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Dissolved Metals in Seawater						
Arsenic (As)	EPA 1640 RP	0.0395	0.375	μg/L		
Cadmium (Cd)	EPA 1640 RP	0.0203	0.1	μg/L		
Copper (Cu)	EPA 1640 RP	0.078	0.25	μg/L		
Lead (Pb)	EPA 1640 RP	0.02	0.1	μg/L		
Nickel (Ni)	EPA 1640 RP	0.0751	0.25	μg/L		
Selenium (Se)	EPA 1640 RP	0.156	1.5	μg/L		
Silver (Ag)	EPA 1640 RP	0.01	0.1	μg/L		
Zinc (Zn)	EPA 1640 RP	0.139	0.5	μg/L		
Total Cn	SM 4500-Cn E	0.007	0.02	mg/L		
Dissolved Hg	EPA 1631 E	0.0834	0.5	ng/L		

5. Reporting

Reporting for this project will include water quality results delivered to the City after each round of sampling and a final report summarizing the monitoring effort and the water quality results from the project. The individual sampling round results will be delivered to the City as soon as made available from the laboratories and WWTF personnel. The final report will first be made available to the City in draft form for their input. A final version will then be produced by Underwood Engineers and delivered to the City for project close out.